

Review

Review on Melt Cast Explosives

Pasupala Ravi,^a Dilip M. Badgujar,^{*b} Girish M. Gore,^b Surya P. Tewari,^a Arun K. Sikder^{*b}

^a Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad Hyderabad 500046, India

^b High Energy Materials Research Laboratory (HEMRL), Pune 411 021, India
e-mail: ak_sikder@yahoo.com; dmbadgujar@rediffmai.com

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Abstract

A systematic overview of melt cast explosives is given. The research on melt cast explosives over several decades can be divided into three broad areas: (i) aromatic compounds with C-CH₃, N-CH₃, OCH₃, C-NO₂, N-NO₂ and ONO₂ groups, (ii) improved synthesis of compounds, which are currently used in formulations or which have shown promise for such use and (iii) the preparation of melt cast formulations with various compositions. Exudation, high volume change from liquid to solid, super cooling, irreversible growth, fragility and unpredictable sensitivity are the disadvantages of existing melt cast formulations.

Keywords: Heat of Formation, Density, Sensitivity, Detonation Velocity, Detonation Pressure

1 Introduction

Melt cast explosives are used in mortars, grenades, artillery shells, warheads and antipersonnel mines. Most of the compounds were synthesized by liquid-phase nitration using nitric acid-sulfuric acid, fuming nitric acid or nitric acid-acetic anhydride [1,2]. For special compounds, syntheses in several steps and nitration with nitrous oxides and metal nitrates were also reported. Nevertheless, by-products, isomeric compounds and acid residues need to be removed to obtain the pure, stable and desired product. An ideal melt cast explosive or its formulations should have the following properties: (i) melting point 70 to 120 °C, (ii) low vapor pressure (low inhalation toxicity), (iii) a sufficient charge separation between melting point and the start of chemical decomposition, (iv) no shrinking and cracking on cooling, (v) no separation from the shell or casing, (vi) higher density and better explosive performance, (vii) no premature detonation and (viii) greener synthesis. Unfortunately, these characteristics are often

contradictory to each other. For example, most melt cast compounds or their formulations showing high performance are prone to undergo cracking or shrinking on cooling. However, compounds with good thermal stability and insensitivity usually exhibits poor detonation performance [3–5].

The existing melt cast technology is based on TNT, DNAN, TNAZ and ADN. Usually, formulations are processed in large anchor melt cast kettles heated at 80 to 120 °C with hot water or steam mixing ingredients under low shear (1000 to 2500 Pa s). After mixing, the molten explosive is poured into a mold or projectile and allowed to cool and solidify. Some times after the binder a molten, energetic oxidizer such as RDX, HMX, TNAZ or NTO is added. Over the past few decades a large number of publications describing preparation of various melt cast explosives and their formulations appeared, however no comprehensive review of these materials is currently available. Our continuing interest in this subject prompts us to overview this burgeoning field and the present review covers the chemistry of melt cast explosives and their formulations.

2 Melt Cast Explosives and Their Formulations

2.1 2,4,6-Trinitrotoluene (TNT)

It has a long history as military and industrial explosive. TNT was first synthesized in 1863. It is by no means a high performance explosive. The direct nitration of toluene to TNT using nitric acid-sulfuric acid is not industrially feasible. Usually, nitration of toluene to TNT is conducted in two or three steps. The mixed acid from previous di- and tri-nitrate ions is reformed with nitric acid and used for mononitration and dinitration respectively.

The mixed acid containing up to 7% water is effective as oleum-nitric acid mixtures for nitrating toluene to dinitrotoluene yields being >99% after 1 h [1]. Toluene was nitrated to dinitrotoluene with potassium nitrate in sulfuric acid at -10°C and also with nitric acid-triflic acid at lower temperatures. The nitration of dinitrotoluene to TNT requires mixed acid fortified with oleum at elevated temperature.

The performance data of TNT are: $\rho = 1.64 \text{ g cm}^{-3}$, $D = 6.94 \text{ km s}^{-1}$ and $P = 29 \text{ GPa}$. The combination of high chemical stability, moderate insensitivity to impact and friction and a low melting point (80.8°C) to permit melt casting of charges make TNT suitable for use in munitions [6–8]. In modern applications, particularly mining and building demolition, TNT has replaced nitroglycerine (NG). Mixtures of TNT and ammonium nitrate (AN) were widely used as Amatols in the past. Torpex (42% RDX, 40% TNT, 18% Al), Pentolite (50% PETN, 50% TNT), Ammonite (80% NH_4NO_3 , 20% TNT) Octol (70–75% HMX, 25–30% TNT) and TNTO (50% TNT, 50% NTO) are well known melt cast formulations [8,9]. However, such compositions are weak and brittle prone to cracking, exudation and dimensional instability in response to thermal cycling. Alternatives to RDX/TNT compositions have also been made to improve the performance, sensitivity and material properties of existing formulations.

2.2 2,4-Dinitroanisole (DNAN)

DNAN is a less toxic, less sensitive and Class 4.1 flammable solid, which is used as replacement for TNT in melt cast formulations [3]. It was used as a bomb filling component during World War I & II. It has a slightly lower performance ($D = 5.60 \text{ km s}^{-1}$ and $P = 7.02 \text{ GPa}$) compared with TNT however, its use in melt cast formulations is presently undergoing renaissance for various applications. The direct nitration of phenol or anisole to DNAN is not feasible industrially. It is synthesized in higher yields by methoxylation of 1-chloro-2,4-dinitrobenzene. It can also be synthesized by the nitration of *p*-nitroanisole or *o*-nitroanisole. The impact and friction sensitivities of DNAN are 220 cm and 170 N respectively [1,3]. It is highly oxygen deficient ($\Omega = -97.9\%$). It has a melting point of 94.5°C and a density of $\rho = 1.34 \text{ g cm}^{-3}$.

The melting point of DNAN can be depressed by several degrees by the addition of small quantities of melt soluble additives such as *N*-methyl-4-nitroaniline (MNA), which provides a medium more suited to typical melt cast process [9]. It was main charge ingredient in Amatol 40 (50% DNAN, 35% AN, 15% RDX) in the warhead of V-1 flying bombs during World War II [1,8]. DNAN-based formulations such as PAX-21, PAX-25, PAX-33, PAX-34, OSX-1, OSX-3, OSX-7 and OSX-8 were used for munitions [10–14]. The impact and friction sensitivities of ARX-4027 (40% DNAN and 60% RDX) are slightly lower than Comp B [13]. The viscosity and settling properties of ARX-4027 are promising compared with Comp B. Similarly, PAX-21 showed lower shock sensitivity compared with Comp B. The low shock sensitivity RS-RDX is not retained when dissolved in molten DNAN however, non-RS-RDX gives slightly higher detonation pressure.

Trinitroanisole is a low sensitive explosive with its performance intermediate between TNT and picric acid [14]. 2,4,6-trinitroanisole (TNAN) has a low m. p. of 68°C and thus it has a limited practical importance [3]. It produces skin eczemas and is not safe physiologically.

2.3 Tris Aziridine Melamine (Tris-X) and Methyl Tris Aziridine Melamine (Methyl Tris-X)

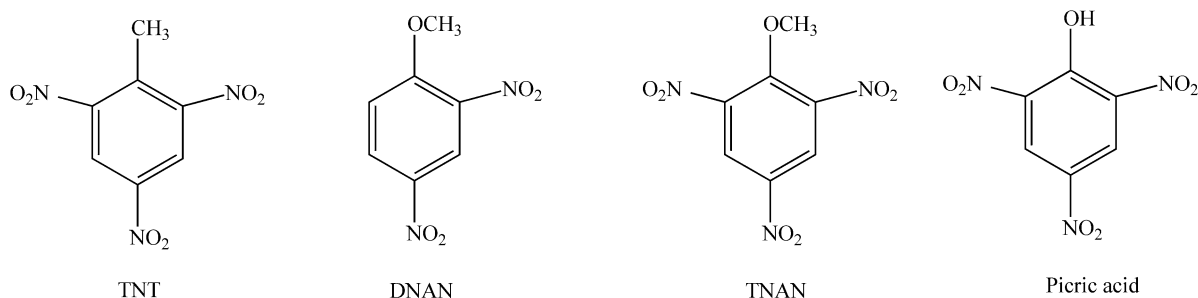
Tris-X and Methyl Tris-X have both nitramine and nitrate ester groups. Aziridine ring-opening nitration has been used to synthesize Tris-X and Methyl Tris-X.

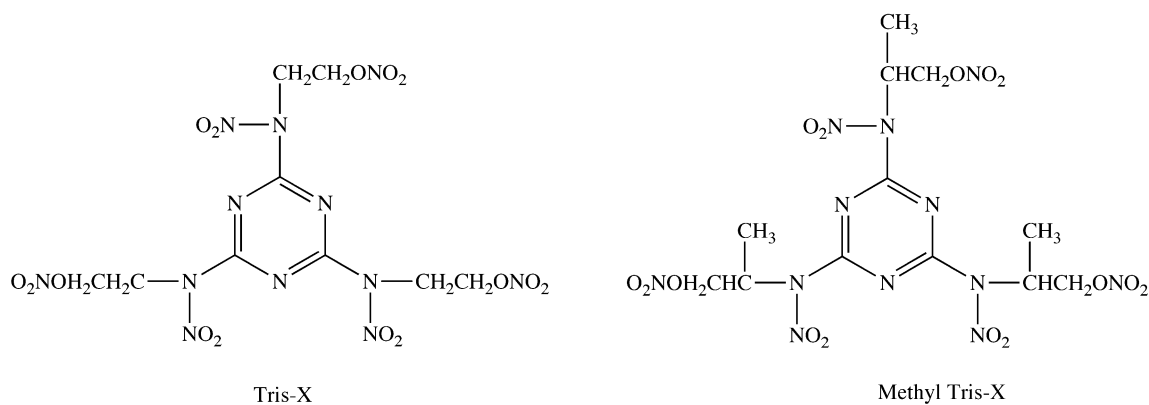
Tris-X was obtained by reaction of 2,4,6-tris(aziridino)-1,3,5-triazine with dinitrogen pentoxide in chloroform or dichloromethane at sub-ambient temperature (-30°C) [15,16].

Tris-X has a melting point of 69°C , its performance data are: $\rho = 1.73 \text{ g cm}^{-3}$, $D = 8.7 \text{ km s}^{-1}$, $P = 30 \text{ GPa}$ and $h_{50\%} = 57 \text{ cm}$. Thermal stabilities of Tris-X and Methyl Tris-X are marginally acceptable unlikely to be used for munitions.

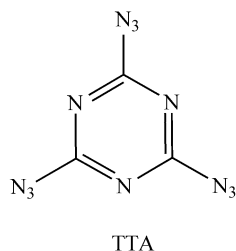
2.4 2,4,6-Triazido-1,3,5-triazine (TTA)

It is a heavy metal free polyazido compound containing only carbon and nitrogen. It has high impact and friction





sensitivities and the performance is comparable to lead azide and lead styphnate [3]. TTA was synthesized by treatment of cyanuric chloride with sodium azide in acetone.



It has a lower density than lead azide thus it cannot be packed as much as lead azide. It has a density of $\rho = 1.54 \text{ g cm}^{-3}$, a melting point of 94°C , a decay point of 187°C and a D value of 5.68 km s^{-1} [17–19]. However, triazidopyrimidine melts at 103°C , decomposes at 195°C , its density amounts to 1.55 g cm^{-3} and its heat of formation to $1087.4 \text{ kJ mol}^{-1}$ compared with 2,4,6-triazido-1,3,5-triazine [20].

2.5 4,4'-Dinitro-3,3'-bifurazan (DNBF)

Coburn [21,22] synthesized DNBF by oxidizing 4,4'-diamino-3,3'-bifurazan (DABF) with 90% hydrogen peroxide in trifluoroacetic acid. Sheremetev et al. [23] devel-

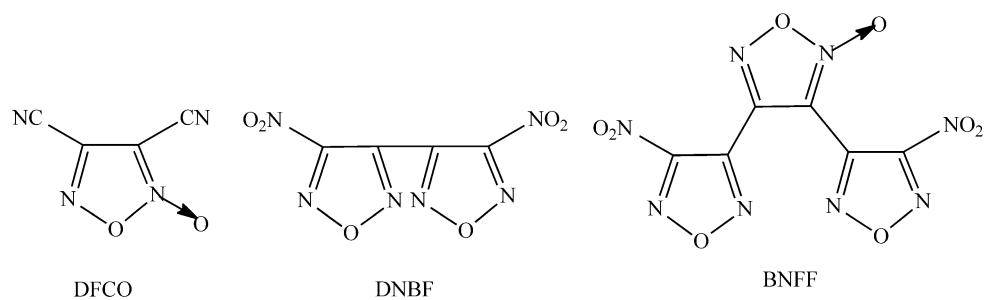
oped an alternative synthesis, which had several advantages over Coburn synthesis. The thermodynamic data of DNBF are: m.p. = 85°C , $\rho = 1.85 \text{ g cm}^{-3}$, $D = 8.8 \text{ km s}^{-1}$ and $P = 35.6 \text{ GPa}$.

The low melting point and promising explosive properties make DNBF a very attractive melt cast explosive. It has $h_{50\%} = 12 \text{ cm}$, which is similar to pentaerythritol tetranitrate (PETN) thus demanding stringent safety measures during synthesis and handling.

2.6 1,2,5-Oxadiazole-3,4-dicarbonitrile-2-oxide or 3,4-Dicyanofuroxan (DFCO)

Homewood et al. [24] synthesized DFCO nitrating cyanoacetic acid with nitric acid in trifluoroacetic acid or trichloroacetic acid at 40°C for 2 h. It was also obtained by diazotization of aminofurazans bearing the second substituent. Treatment of 3-amino-4-nitrofurazan with 3 to 6 equivalents of sodium nitrite in sulfuric acid/acetic acid at 35°C gave <8% yield [25]. Treating 3-aminofurazab-carboxylic acid and 3-amino-4-nitrosfurazan under similar conditions gave 22% and 72% yields respectively.

DFCO has been used as a substitute to TNT, nitroglycerine and similar explosives. It has a considerable amount of energy. It is extremely stable and safe being insensitive to heat and to impact. Low melting point, stability, detonation velocity and impact sensitivity makes DFCO an attractive explosive for forming complex shaped geometries.



2.7 3,4-Bis(3-nitrofurazan-4-yl)furoxan (BNFF or DNTF)

BNFF is a new energetic oxidizer with higher energy and good thermal stability and less sensitive to impact. It was synthesized by nitration of *C,N*-bis(trimethylsilyl) derivative of 3-amino-4-methylfuran with nitrogen oxides [26]. The oxidation of 3,4-bis(3-aminofurazan-4-yl)furoxan (BAFF) with 96% H₂O₂ and TFAA gave BNFF in 50% yield. BAFF was hardly converted into BNFF with 30% H₂O₂ and H₂SO₄ in the presence of various additional oxidants. The reaction with 60% H₂O₂ and TFAA proceeded to give BNFF in moderate yield. Lim et al. [27] have improved the yields starting from malonitrile and suggested for large scale production.

It has a density of $\rho = 1.937 \text{ g cm}^{-3}$ and a D value of 9.25 km s^{-1} , which are superior compared with HMX [28–30]. It is under consideration as a potential candidate for possible use as the ingredient in melt-pour formulations [31,32].

2.8 1-Methyl-2,4,5-trinitroimidazole (MTNI)

Cho et al. [33] synthesized MTNI from imidazole via a five step sequence of reactions. Damavarapu et al. [34] have recently developed several methods to synthesize MTNI in higher yields starting from 4-nitroimidazole. The direct nitration of 1-methylimidazole with nitronium tetrafluoroborate-nitromethane at 105 °C for 2 h gave 23% yield. The nitration of 1-methyl-2,4-dinitroimidazole with nitric acid-sulfuric acid mixture or nitric acid under microwave irradiation gave lower yield. Jadhav et al. [35] synthesized MTNI from polyiodoimidazole refluxing in fuming nitric acid.

The sensitivity of MTNI ($h_{50\%} = 100 \text{ cm}$, $F = 252 \text{ N}$) is intermediate between RDX and TNT and the performance ($D = 8.80 \text{ km s}^{-1}$, $P = 35.58 \text{ GPa}$) is similar to RDX. In addition, owing to its melting point of 82 °C and its promising density of $\rho = 1.78 \text{ g cm}^{-3}$, MTNI is under consideration as a novel candidate for inclusion in formulations.

2.9 3,4-Dinitropyrazole (DNP)

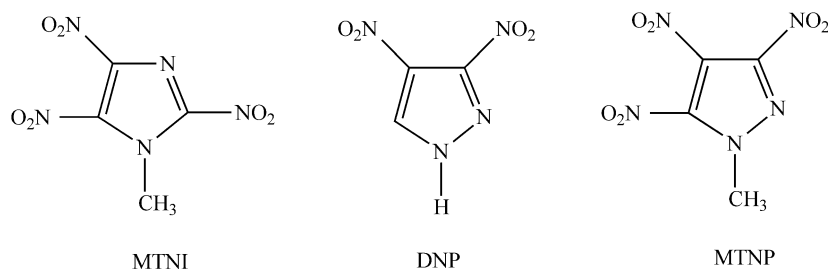
Janssen et al. [36,37] synthesized DNP from 3-nitropyrazole. In turn, 3-nitropyrazole was obtained by heating *N*-nitropyrazole to reflux in anisole at 145 °C for 10 h or in benzonitrile at 180 °C for 3 h. The intramolecular migra-

tion of nitro group can be visualized as a [1,5] sigmatropic shift to 3*H*-pyrazole followed by the fast tautomerization. The isomerization reaction was also performed at temperatures 120–180 °C in *n*-decane, mesitylene, nitrobenzene, *N*-methylformamide and propylene glycol [38].

Latypov et al. [39] improved the yield treating 3-amino-4-nitropyrazole in presence of excess nitrite ion. Katritzky et al. [40] obtained DNP in 41% yield by nitrating pyrazole with nitric acid-trifluoroacetic anhydride at room temperature for 12 h. We have obtained higher yield of DNP by heating 3,4-diiodopyrazole in nitric acid to reflux [41]. In turn, 3,4-diiodopyrazole was obtained by the iodination of pyrazole with I₂/KI in ammonium hydroxide [42]. The nitration of 4-nitropyrazole was unsuccessful rather we recovered quantitative amount of starting compound. The rearrangement of 1,3-dinitropyrazole at 180 °C for 3 h in benzonitrile gave 3,5-dinitropyrazole (85 to 90%) as well as unreacted 3-nitropyrazole (10 to 15%). However, 1,4-dinitropyrazole in the same conditions gave a mixture containing 3,5-dinitropyrazole, unaltered 1,4-dinitropyrazole and 4-nitropyrazole [39]. The thermodynamic properties of DNP are: melting point = 86 °C, $\rho = 1.81 \text{ g cm}^{-3}$, $\Delta_f H = 120.1 \text{ kJ mol}^{-1}$, $D = 8.24 \text{ km s}^{-1}$, and $P = 28.80 \text{ GPa}$ [43,44].

2.10 1-Methyl-3,4,5-trinitropyrazole (MTNP)

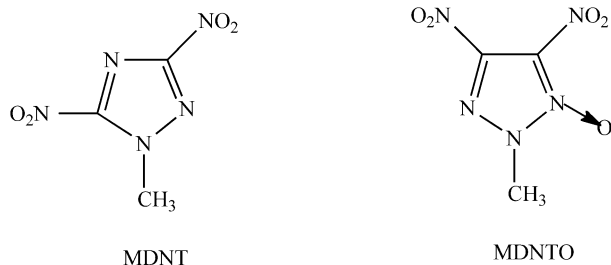
Herve et al. [45,46] synthesized MTNP, a new derivative of 3,4,5-trinitropyrazole (TNP) from sodium trinitropyrazolate using methyl iodide in acetonitrile. In turn, TNP was obtained in 93% and 37% yields from 4-amino-3,5-dinitropyrazole and 5-amino-3,4-dinitropyrazole respectively using diperoxysulfuric acid. A very high yield (94%) of TNP was obtained using a mixture of nitric acid and 20–30% oleum at 100 °C for 1 h. 3,4,5-Triiodopyrazole and 3,4,5-triiodo-1-methylpyrazole were selectively nitrodeiodinated to 3,4,5-trinitropyrazole and 1-methyl-3,4,5-trinitropyrazole in higher yields using nitric acid [41]. 1-Methyl-3,5-dinitropyrazole melts at 62 °C and may serve as a precursor to synthesize MTNP [47]. The nitration of 1-methyl-3,5-dinitropyrazole using nitric acid-sulfuric acid at 100 °C for 30 minutes gave 75% yield. 1-Methyl-3,4-dinitropyrazole melts at 21 °C and thus may serve as an energetic liquid [48,49]. Our attempts to nitrate 1-methyl-3,4-dinitropyrazole have been found to be unsuccessful [42]. The thermodynamic properties of



MTNP are: melting point = 91 °C, dec. point = 256 °C, $\rho = 1.83 \text{ g cm}^{-3}$, $D = 8.96 \text{ km s}^{-1}$, and $P = 33.54 \text{ GPa}$ [45].

2.11 1-Methyl-3,5-dinitro-1,2,4-triazole (MDNT)

MDNT was synthesized by the nitration of guanazole with sodium nitrite-sulfuric acid. It was then treated with dimethyl sulfate or iodomethane to obtain 1-methyl-3,5-dinitrotriazole in 45% yield [50].



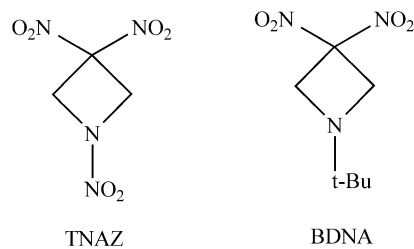
It has a melting point of 98 °C and a density of $\rho = 1.676 \text{ g cm}^{-3}$. The performance properties are close to those of Comp B. The impact and friction sensitivities are > 100 cm and 252 N respectively.

2.12 2-Methyl-4,5-dinitro-1,2,3-triazole-3-oxide (MDNTO)

The nitration of 2-methyl-1,2,3-triazole-3-oxide with nitric acid-sulfuric acid gave 2-methyl-4,5-dinitro-1,2,3-triazole-3-oxide [50]. In turn, *N*-oxide was obtained by the condensation of glyoxal, hydroxylamine and methyl hydrazine followed by the oxidation with hydrogen peroxide and copper sulfate. It has a melting point of 132 °C, a decay point of 256 °C and a density of $\rho = 1.73 \text{ g cm}^{-3}$. It has an impact sensitivity of 80 cm and the performance exceeds that of MDNT.

2.13 1,3,3-Trinitroazetidine (TNAZ)

TNAZ is a widely studied cyclic nitramine suitable for applications as a melt cast explosive as well as energetic plasticizer. TNAZ built on highly strained ring structures which add approximately 155 kJ mol^{-1} to the internal energy. It was synthesized by numerous routes and most of the methods offer low yields. Several efforts have been received to improve the yield by reducing the number of steps. In 1984, Archibald et al. [51] synthesized TNAZ for the first time at Fluorochem starting from *tert*-butylamine with epichlorohydrin. Efforts have also been made to decrease reaction time and to increase yield. Katrizky et al. [52] obtained superior yields compared with Archibald's procedure. Axenrod and co-workers [53–56] used 3-amino-1,2-propanediol as a starting material to avoid the utilization of epichlorohydrin. Marchand et al. [57,58] synthesized TNAZ using 2-amino-1,3-propanediol proceeded through 1-azabicyclo[1.1.0]butane.



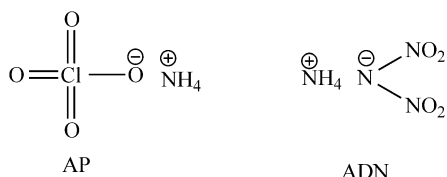
Coburn et al. [59,60] improved the synthesis making it more amenable to scale-up by condensing tris(hydroxymethyl)nitromethane with *tert*-butylamine and formaldehyde. The *tert*-butyl-5-hydroxymethyl-5-nitrotetrahydro-1,3-oxazine formed in the above step was treated with aqueous hydrochloric acid to yield 2-*tert*-butylaminomethyl-2-nitro-1,3-propanediol hydrochloride, which was cyclized under Mitsunobo conditions to 1-*tert*-butyl-3-hydroxymethyl-3-nitroazetidine hydrochloride. Then it was treated with sodium hydroxide and oxidatively nitrated to yield 1-*tert*-butyl-3,3-dinitroazetidine (BDNA). The nitrolysis of BDNA with ammonium nitrate and acetic anhydride gave TNAZ. Hiskey et al. [61] synthesized 3,3-dinitroazetidine and its various salts such as nitrate, dinitramide, 3,5-dinitrotriazolate, 4,4',5,5'-tetranitrobiimidazolate, 2,4-dinitroimidazolate and 3-nitro-5-hydroxytriazolate. Hayashi et al. [62] improved the yield starting from 12,-dibromopropyl-3-amine hydrobromide.

The thermodynamic properties of TNAZ are: $\Omega = -16.70\%$, m.p. = 101 °C, $\rho = 1.84 \text{ g cm}^{-3}$, $D = 8.73 \text{ km s}^{-1}$, $P = 37.2 \text{ GPa}$, and $h_{50\%} = 21 \text{ cm}$ [63]. It has a higher performance than RDX and HMX [64]. TNAZ potentially offers a 30–40% improvement in the detonation performance as a TNT replacement in Comp B [65,66]. It is more shock sensitive than the formulations based on HMX but less sensitive than PETN mixtures. To improve the mechanical strength and better resistance to impact of TNAZ/CAB formulations, thermoplastic elastomeric binders such as BAMO/AMMO, HYTREL and ESTANE are added [67]. The shock sensitivity can be reduced by adding 5–25% of *N*-methyl-4-nitroaniline, which influences the nucleation during solidification. High vapor pressure, volume contraction and formation of shrinkage cavities (10–12% porosity) on cooling are minor disadvantages. The excessive vapor pressure and charge porosity can be reduced by the addition of *N*-methyl-4-nitroaniline to the melt.

2.14 Ammonium Dinitramide (ADN)

ADN is an eco-friendly energetic oxidizer with a large amount of available oxygen for combustion alternative to ammonium perchlorate (AP). The use of ADN in place of AP increases energy and burning rate of propellant formulations. It has potential applications as a rocket propellant ingredient, a melt cast underwater explosive and as a cationic phase transfer agent. The absence of carbon and chlorine in its structure reduces the radar signature in the exhaust plume of ADN-based propellants in rock-

ets/missiles [68–70]. The space shuttle can lift 8% more mass into orbit by using ADN compared with AP. The amount of free oxygen in ADN is high such that it can be used for formulations with powerful reducing agents like aluminum, magnesium, and boron. It has a melting point of 92 °C and a density of $\rho = 1.82 \text{ g cm}^{-3}$. It is more stable or less sensitive compared with alkyl dinitramides [71,72] and the stability is attributed to the delocalized negative charge that stabilizes N–NO₂ bonds to become susceptible to rupture [73].



Numerous routes to synthesize dinitramide anion have been reported [74–84], however many are not feasible for large scale production. Hatano and co-workers [85,86] reported a clean and safe method for the synthesis of ADN starting from urea. Stern et al. [83] nitrated methyl and ethyl carbamate with nitric acid-acetic anhydride at 0 °C to mononitro compound which is followed by treatment with ammonia to give methyl or ethyl *N*-nitrocarbamate. It was further nitrated with N₂O₅ at –48 °C in dichloromethane and afterwards treated with ammonia to obtain dinitramide. Alkyl carbamate nitrating with nitric acid-acetic anhydride at 0 °C to give *N*-(alkoxycarbonyl)*N*-nitramide, which is treated with ammonia to produce ammonium nitrourethane. It is nitrated with NO₂BF₄ to give dinitrourethane, which is further treated with ammonia to ammonium dinitramide [87]. The nitration of bis(2-cyanoethyl)amine with Ac₂O/HNO₃ at 0 °C followed by alkaline decyanoethylation and further nitration with NO₂BF₄ to give 60% yield of AND [88].

ADN is relatively easy to cast when 1% MgO is used as a stabilizer [89]. The unstabilized ADN cannot be melt cast due to excessive gas generation rate and risk of initiation. It shrinks (14% of its volume) more than TNT while solidifying thus making it more difficult to obtain a void free, crackless and tension free casting. Cast ADN has a higher density than the pressed ADN and also in

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contrast to TNT based compositions. Al powder can also be mixed up to 35% without problems and the mixtures are easier to cast than nitramide alone.

2.15 Triaminoguanidine Dinitramide (TAGDN)

TAGDN was synthesized from guanidine dinitramide (GUDN) by heating to reflux with equivalent amounts of hydrazine hydrate in boiling dioxane. In turn, GUDN was precipitated by addition of ADN to concentrated aqueous solution of guanidine nitrate [90–92].

It has a melting point of 85 °C, a heat of formation value of $\Delta_f H = +184 \text{ kJ mol}^{-1}$ and a density of $\rho = 1.57 \text{ g cm}^{-3}$. TAGDN starts to decompose in the range of 150–160 °C with a heating rate of 10 K min^{–1}. Due to the low flame temperature that is preferred in gun, TAGDN seems better suited as a component in gun propellants. Due to high sensitivity, TAGDN should be handled with care and it is questionable if it can be used in solid propellants. The water solubility is known to be very low (10%) and hence TAGDN is less attractive than ADN in liquid monopropellants [92].

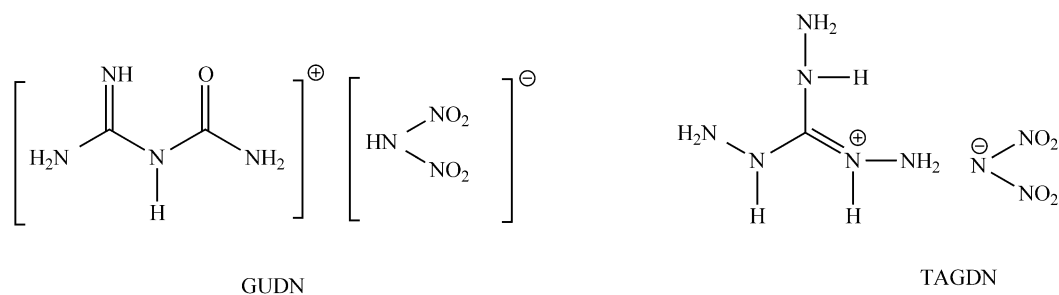
2.16 Tetranitrate Ester (TNE)

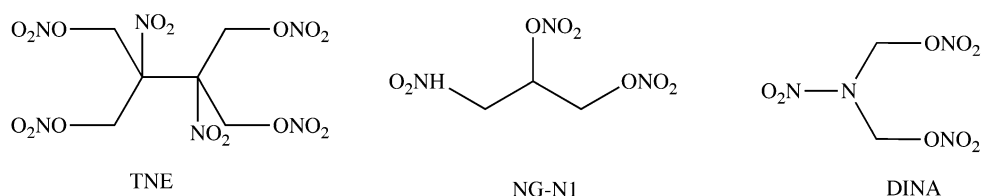
Chavez et al. [93] synthesized tetranitrate ester (TNE). The nitration of tetraol with acetyl nitrate in acetic acid gave 85% of tetranitrate ester. TNE melts at 86 °C and decompose at 141 °C, respectively. The heat of formation and heat of decomposition are –371 kJ mol^{–1} and 818 J g^{–1}, respectively.

The thermodynamic data of TNE are: $\rho = 1.92 \text{ g cm}^{-3}$, $D = 9.1 \text{ km s}^{-1}$ and $P = 40 \text{ GPa}$. These are higher compared with HMX. Due to its low melting point, it can be melted and poured into molds, a much easier process for the production of explosive components. It also offers the possibility of use as a high energy plasticizer or double base propellant ingredient. The sensitivity towards shocks, friction and sparks is equivalent to nitropenta and can be served as highly energetic softener for other explosives.

2.17 1-Nitramino-2,3-dinitroxypropane (NG-N1)

Altenburg et al. [94] reported the synthesis and explosive properties of 1-nitramino-2,3-dinitroxypropane. It is a





new primary nitramine, which belongs to the family of nitroglycerine. It was synthesized in high yield and purity starting from 1-amino-2,3-propanediol. NG-N1 melts at 66 °C and decomposes at 173 °C. It is unique in its thermal behavior and so far the only primary nitramine which can be molten without decomposition. The thermodynamic data of NG-N1 are: $\rho = 1.80 \text{ g cm}^{-3}$, $D = 8.84 \text{ km s}^{-1}$ and $P = 32.60 \text{ GPa}$, which are similar to RDX. Due to hydrogen bonding the sensitivity of NG-N1 is reduced (14 J) compared to that of nitroglycerine (0.2 J).

2.18 N-Nitrodiethanolamine Dinitrate (DINA)

DINA is a powerful explosive which can be casted into charges. It was synthesized from diethanolamine and nitric acid with acetic anhydride in the presence of hydrochloric acid. The nitration product is stabilized by boiling in water, followed by dissolution in acetone and reprecipitation with water. The thermodynamic data of DINA are: mp: 51.3 °C, $\rho = 1.488 \text{ g cm}^{-3}$, $D = 7.58 \text{ km s}^{-1}$ and $P = 28.60 \text{ GPa}$ [3]. It is a satisfactory gelatinizer or plasticizer for nitrocellulose. It is also a powerful explosive similar to RDX and PETN. Double base propellants based on DINA instead of nitroglycerine named as Alabanite known in the literature.

2.19 Bis(2,2-dinitropropyl)fumarate (FUM) and 2,2-Dinitropropyl-4,4-dinitropentanoate (PENT)

2,2-Dinitropropyl-4,4-dinitropentanoate and bis(2,2-dinitropropyl)fumarate were used as binders, oxidizers and explosives in composite propellants. FUM melts at 84 °C and PENT melts at 95 °C. FUM and PENT have impact sensitivities of 276 and 320 cm respectively [1,3].

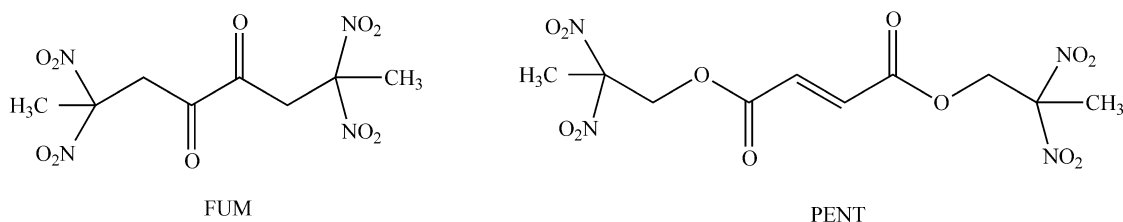
The simplest composites containing FUM or PENT mixed with a metal fuel such as aluminum, magnesium, boron, hafnium, zirconium or alloys in the form of powders or flakes are known [95]. Aluminum and magnesium are the preferred fuels in the compositions. The compo-

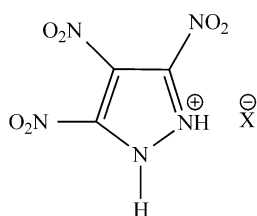
site comprises 73–85 % of FUM or PENT and 27–15 % of metal fuel. FUM or PENT can be used alone or in combination with inert melt castable thermoplastic elastomer (TPE) diluents. TPE diluents are added to improve the physical properties of the binder. The addition of TPE reduces the energy density of the binder and thus explosives. Based on the weight of binder, the inert TPE from 1–10 % is added to the binder/metal fuel mixture. TPE diluents are preferably based on ABA type or AP type block copolymer where A represents a polystyrene (hard) block and B represents an elastomeric (soft) block such as polybutadiene, polyisoprene, polyethylenebutylene, polyacrylate, polyether and so on. The viscosity ingredients such as polyterpene, glycerol esters of tall oil rosins, mineral oils, hydrogenate castor oils or olefinic oils are added to the block copolymer to lower its viscosity at the process temperature so that conventional, low-cost, low-shear mixtures are used to prepare the explosive. It is known that RDX increases the impact sensitivity from 276.1 cm (for FUM) to 70.1 cm (for ARFUM) thus the explosive composition. ALPENT (73 % PENT and 27 % Al), a simple melt cast composite has the following thermodynamic data: $\rho = 1.74 \text{ g cm}^{-3}$, $Q = 7.686 \text{ kJ g}^{-1}$ and $h_{50\%} = 320 \text{ cm}$. It was shown that the impact sensitivity of PENT remained unchanged (320 cm) after mixing with 27 % of Al [95].

2.20 Energetic Salts

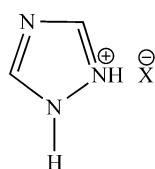
Nitroazoles can be paired with anions such as nitrate, perchlorate and dinitramide to form low-melting energetic materials allowing them to be readily castable at moderate processing temperatures.

The energetic salts often have advantages over nonionic molecules since these salts tend to exhibit lower vapor pressure and higher densities than their atomically similar nonionic analogues [96–104]. The salts of 1,2-diazole, 1,3-diazole, 1,2,4-triazole, 1,2,3-triazole, 1-amino-1,2,4-triazole, 4-amino-1,2,4-triazole, 4-methyl-1-amino-1,2,4-tria-

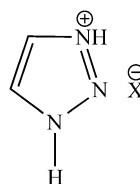




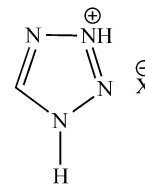
3,4,5-Trinitropyrazolium salts



1,2,4-Triazolium salts



1,2,3-Triazolium salts



1,2,3,4-Tetrazolium salts

where, $X = \text{NO}_3^{\ominus}, \text{ClO}_4^{\ominus}, \text{N}(\text{NO}_2)_4^{\ominus}$

zole, 1,2,3,4-terazole were made in high yield by the simple reaction of one equivalent azole and one equivalent of the strong acid of the energetic anion desired. Nitrate, perchlorate and dinitramide salts have low melting points 70 to 110 °C. The synthesis of non-protonated salts of ethylene bisoxyamine were made by the reaction of one equivalent of ethylene bisoxyamine with one equivalent of the strong acid of the desired energetic anion. Ethylene bisyamine and its nitrate, perchlorate and dinitramide salts have lower melting points 76, 137, 59 °C respectively [105,106]. Traditional energetic compounds may be incorporated to enhance performance of these salts and to create formulations that are analogous to Comp B, Amatol, Tritonal and Torpex. Other energetic ingredients include RDX, HMX, CL-20, PETN, NQ and/or oxidizing salts such as AP, ADN, AN, LiN, or LiP.

1-Methyl-4-amino-1,2,4-triazolium perchlorate (MATP) has melting point almost identical to TNT and its high heat of formation and better oxygen balance should lend improved performance properties.

3 Conclusions

The current melt cast technology is based on the energetic binders TNT, DNAN, TNAZ, and ADN. Exudation, high volume change from liquid to solid, super cooling, irreversible growth, and unpredictable sensitivity have been found to be disadvantages of existing melt cast formulations. Explosive compositions are weak, brittle materials subject to cracking and are prone to exudation and dimensional instability in response to thermal cycling. Alternatives to RDX, HMX, or NTO/TNT compositions with a binder/desensitizer and polymer bonded explosives suspended in a matrix of binder improve the performance, sensitivity and material properties.

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